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(54) Title: A SURFACE ACTIVE COMPOSITION CONTAINING AN ACETAL OR KETAL ADDUCT		
(57) Abstract <p>Disclosed is a composition which comprises an acetal or ketal adduct of a monohydroxyl-terminated polyoxyalkylene. Such compositions find value as components in cleaning methods, methods of controlling foam formation, drilling muds, and in formulations for use as cosmetics, pharmaceuticals and pesticides, where modification of surface active properties may be desired.</p>		

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A SURFACE ACTIVE COMPOSITION
CONTAINING AN ACETAL OR KETAL ADDUCT

5 This invention relates to surfactants and more particularly to compositions which comprise a polyoxyalkylene acetal or ketal, and a process for preparing the same.

 Products having surface active properties, commonly called surfactants or stabilizing agents, are widely used in many industrial, agricultural and pharmaceutical applications where it is necessary to modify hydrophobic/hydrophilic surface interactions. Frequently employed surfactants include liquid polyoxyalkylene polymers and silicon-based
10 polyoxyalkylene polymers. However, in recent times there has been an increasing awareness of environmental and ecological aspects for many applications, especially where possibility of an accumulation of such surfactants in the environment exists to the potential detriment of established ecosystems. Accordingly, it would be desirable to use a surfactant product which
15 possesses a greater activity and therefore could be deployed in smaller amounts to achieve the same technical result. Use of smaller amounts would lead to a significantly reduced environmental accumulation potential. Alternatively, it would be desirable to use a surfactant which can be more readily biodegraded. In the optimum, it would be desirable to use a surfactant which exhibits a greater activity in the application area and which further has an
20 attractive degree of biodegradability. Certain substances are known from the art to have surfactant activities and additionally exhibit some biodegradability, such substances include ketals and acetals as discussed in the patent document EP-A-512,501. Thus, the preparation of alternative surfactants comprising acetal adducts has been investigated with a view to obtaining an enhanced surfactant activity and eventually enhanced biodegradability. The
25 assessment of surface activity can be conveniently determined by observing the change of surface tension of water with concentration of the adduct. When, upon addition of the adduct, the surface tension of water ceases to change (normally decrease) the critical micelle concentration (CMC) for the adduct has been attained. A lower CMC value is taken as indicating a greater surface activity.

30 In the art, it is known to prepare acetal or ketal products by reacting an alcohol with an aldehyde, or ketone, respectively, in the presence of an acid catalyst. Such procedures are disclosed in various patent documents including GB 1,178,988; EP-A-164,425; EP-A-525,626; DE 33 18 592; DE 34 41 542; U.S. 2,556,559; U.S. Patent 2,840,615; U.S. Patent 4,024,159; and U.S. Patent 4,579,979.

35 In the alternative, acetals or ketals may be obtained by reacting an alcohol with a vinyl ether or olefin. U.S. Patent 3,024,284 discloses a process for the preparation of simple ketals by reacting a lower secondary alcohol with an alpha-unsaturated ether in the presence of an acid catalyst. U.S. Patent 3,931,337 discloses the preparation of multiblock polyacetal

copolymer surfactants by reacting a polyoxyalkylene polymer with a lower alkyl vinyl ether followed by thermal coupling of the acetal-terminated polymers to give the final product. U.S. Patent 3,954,886 discloses the preparation of polyoxyethylene acetal surfactants by the sequential reaction of polyoxyethylene diols with a high molecular weight alkyl vinyl ether followed by a low molecular weight alkyl vinyl ether. U.S. Patent 3,244,753 discloses the preparation of acetals of mono- and polyoxyalkylene glycols with vinyl ethers in the presence of an acid catalyst and specific phosphorus compounds to prevent the formation of colored products. U.S. Patent 2,905,719 discloses the preparation of acetal surfactants by reacting vinyl ethers containing from 8 to 18 carbon atoms with ethoxylated alcohols. German patent DE 22 52 186 discloses the preparation of a surfactant by reacting a polyoxyalkylene polyol, predominantly oxypropylene, with an excess of an alkyl vinyl ether in the presence of an acid catalyst. Despite the seemingly extensive knowledge relating to acetal/ketal surfactants there is still a need to develop alternative products with a view to optimizing activity and/or biodegradability properties.

In one aspect, the present invention is a composition comprising a hydroxyl-terminated polyoxyalkylene and an acetal or ketal characterized in that:

- a) the acetal or ketal, present in an amount of from 1 to 99 percent by weight based on total parts by weight of the composition, is an adduct of a monohydroxyl-terminated polyoxyalkylene; and
- b) the composition exhibits a critical micelle concentration (CMC) in water of less than 25 ppm of water at 25°C.

In another aspect, the present invention is a fatty alcohol alkoxylate composition which contains from 1 to 99 parts per 100 parts by total weight of the composition of an acetal mixture comprising components (a) and (b) wherein said mixture is characterized in that, based on the total parts by weight of (a) and (b) present, it comprises:

- a) from 1 to 99 weight percent of a substance corresponding to Formula (I), and
- $$\begin{array}{c} \text{F} - (\text{AO})_n - \text{O} - \text{CH} - \text{O} - (\text{AO})_n - \text{F} \\ | \\ \text{CH}_3 \end{array} \quad (\text{I})$$
- b) from 99 to 1 weight percent of a substance corresponding to Formula (II),
- $$\begin{array}{c} \text{F} - (\text{AO})_n - \text{O} - \text{CH} - \text{O} - \text{R} \\ | \\ \text{CH}_3 \end{array} \quad (\text{II});$$

wherein F is independently a hydrocarbyl radical having from 6 to 30 carbon atoms; AO is independently a C₂₋₄ oxyalkylene moiety where more than 50 mole percent of the oxyalkylene moiety is a C₂ substance; n is independently a number from 3 to 30; and R is a hydrocarbyl radical having from 1 to 5 carbon atoms.

In yet another aspect the present invention is a process for preparing a fatty alcohol alkoxylate, as mentioned above, characterized in that a monohydroxyl-terminated

polyoxyalkylene or fatty alcohol alkoxylate is reacted, in the presence of an acid catalyst, with an alkyl vinyl ether present in an amount to provide from 0.05 to 0.98 equivalents per hydroxyl group.

In other aspects, this invention relates to the following methods and formulations of industrial relevance using one of the above-mentioned compositions, to modify any hydrophilic/hydrophobic or lipophilic/lipophobic interaction, including:

(i) A method for stabilizing oil or gas well walls which comprises using an invert-emulsion or emulsion drilling mud wherein the invert-emulsion drilling mud contains from 0.5 to 100 percent by weight, and the emulsion drilling mud includes from 0.5 to 50 percent by weight, of one of the above-mentioned compositions.

(ii) A method for controlling foam formation of an aqueous or non aqueous mixture in an environment with free surface turbulence which comprises bringing said mixture into contact with from 0.0001 to 10 percent by weight of one of the above-mentioned compositions. Exemplary of situations where control of foam formation is desirable include the paper, pulp and food processing industries.

(iii) A method for cleaning which comprises bringing a surface to be cleaned into contact with a cleansing agent which includes one of the above-mentioned compositions. Particular examples of such a method are the industrial cleaning methods for dairy or brewery equipment.

(iv) A method for dispersing oil spills on water which comprises treating an oil-contaminated water surface with a dispersing agent that includes one of the above-mentioned compositions.

(v) A method to mercerize textile threads, in particular cellulose-based threads such as for example cotton, by treatment with a caustic solution in the presence of one of the above-mentioned compositions.

(vi) A cleaning formulation, in particular a laundry detergent, which comprises a component being one of the above-mentioned compositions.

(vii) A cosmetic formulation which comprises one of the above-mentioned compositions.

(viii) A pesticide formulation comprising an active component such as a herbicide, insecticide, fungicide, or bactericide, and a further component being one of the above-mentioned compositions.

(ix) A pharmaceutical formulation containing a physiologically active component and a further component being one of the above-mentioned compositions.

The attractive surface activity and biodegradability properties of the composition of this invention allows it to conveniently substitute for many of the nonionic surfactants, especially oxyalkylene adducts of fatty alcohols, presently used in industry.

The composition of this invention comprising a hydroxyl-terminated polyoxyalkylene and an acetal or ketal adduct of a monohydroxyl-terminated polyoxyalkylene exhibits a critical micelle concentration (CMC) in water of less than 25, preferably less than 20, more preferably less than 15, and yet more preferably less than 10 ppm of water at 25°C. Such CMC performance can be obtained with a composition which, based on total parts by weight of the composition, comprises from 1 to 99 percent by weight of adduct, preferably an acetal adduct. Advantageously, the adduct is present in an amount of from 5, more preferably from 10, yet more preferably from 15, and yet still more preferably from 20 weight percent; and preferably up to 95, more preferably up to 90, yet more preferably up to 80, and yet still more preferably up to 60 weight percent. The balance of the composition is a hydroxyl-terminated polyoxyalkylene, and particularly a monohydroxyl-terminated polyoxyalkylene such as, for example, an oxyalkylene derivative of an aliphatic fatty alcohol, optionally unsaturated. The provision of a limited acetal/ketal content of the composition is desirable to provide for an enhanced biodegradability and, a reduction of potential aquatic toxicity. The acetal/ketal content also provides the composition with a better resistance to basic conditions rendering it especially suitable for applications where attractive stability under basic conditions is desirable.

In a preferred embodiment of this invention, the composition comprises an acetal mixture which, based on the total parts by weight of components (a) and (b) present, comprises:

- a) from 1 to 99 weight percent of a first acetal substance corresponding to Formula (I),
- $$\begin{array}{c} \text{F} - (\text{AO})_n - \text{O} - \text{CH} - \text{O} - (\text{AO})_n - \text{F} \\ | \qquad \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \end{array} \quad (\text{I})$$
- and
- b) from 99 to 1 weight percent of a second acetal substance corresponding to Formula (II),
- $$\begin{array}{c} \text{F} - (\text{AO})_n - \text{O} - \text{CH} - \text{O} - \text{R} \\ | \qquad \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \end{array} \quad (\text{II})$$

wherein,

- F is independently a hydrocarbyl radical, optionally unsaturated, having from 6 to 30 carbon atoms;
- AO is independently a C₂₋₄ oxyalkylene moiety, and preferably where more than 50 mole percent of the oxyalkylene moiety is a C₂ substance;
- n is independently a number of from 3 to 30; and
- R is a hydrocarbyl radical having from 1 to 5 carbon atoms.

Further to the first and second acetal substance, the mixture may additionally contain a third acetal substance c rresponding to Formula (III):



with R being as stated for (I) or (II). The third acetal substance may be present in an amount of from 0.1 to 15 weight percent of the total acetal mixture comprising the first, second and third
5 acetal substances.

The acetal mixture advantageously contains the first acetal substance preferably in an amount of from 5, more preferably from 20, and yet more preferably from 40; and preferably up to 95, more preferably up to 80 and yet more preferably up to 60 weight percent. In compliment, the acetal mixture advantageously contains the second acetal substance
10 preferably in an amount of up to 95, more preferably up to 80 and yet more preferably up to 60; and preferably from 5, more preferably from 20, and yet more preferably from 40 weight percent.

To provide for the desired degree of biodegradability, the hydrocarbyl radical F advantageously is a linear group which preferably contains from 8, and preferably up to 25,
15 more preferably up to 18, and yet more preferably up to 15 carbon atoms. Carbon-carbon unsaturation may also be present within the hydrocarbyl radical F.

To provide for the desired degree of surface activity, the hydrophobic/lipophilic nature conferred by the presence of the hydrocarbyl radical F should be complimented by a hydrophilic/lipophobic moiety, in this case the oxyalkylene chain of limited length. For this
20 purpose, the value "n" preferably is from 5, more preferably from 7, and preferably up to 20, and more preferably up to 12.

In a highly preferred embodiment, the hydrocarbyl radical F contains from 8 to 12 carbon atoms, and the value "n" is from 7 to 12.

The hydrocarbyl radical R can be any (cyclo) alkane. For reasons of commercial
25 availability and convenience of handling liquid reactants, the hydrocarbyl radical R preferably comprises from 1 to 5 carbon atoms and advantageously is a C₄ or C₅ radical, including the n- or i-isomers of butyl or pentyl radicals.

The remaining part of the composition is a hydroxyl-terminated polyoxyalkylene which is a polyol or, preferably, a monohydroxyl substance. When the hydroxyl-terminated
30 polyoxyalkylene is a monohydroxyl substance, it is advantageously an oxyalkylene derivative of a fatty alcohol having the general formula:



wherein F, AO, and n are as described above.

As mentioned, this invention also relates to a process for the preparation of the
35 above-described composition comprising a ketal, or preferably acetal, adduct by reacting a limited amount of an alkyl vinyl ether with a monohydroxyl-terminated polyoxyalkylene in the presence of an acid catalyst. The amount of alkyl vinyl ether present in the process is up to a

stoichiometric equivalent per hydroxyl group of the monohydroxyl-terminated polyoxyalkylene. Advantageously, the amount of vinyl ether is from 0.05, preferably from 0.1, more preferably from 0.15, and yet more preferably from 0.2; and preferably up to 0.98, more preferably up to 0.95, yet more preferably up to 0.8, and still more preferably up to 0.75 equivalents per hydroxyl group of the polyoxyalkylene. It is presently understood that the alkyl vinyl ether reacts with the monohydroxyl-terminated polyoxyalkylene to provide an acetal corresponding to Formula (II) which, under the acidic process conditions and elevated temperature, subsequently undergoes transacetalization to provide acetal corresponding to Formula (I) and Formula (III). The ability for a transacetalization reaction to occur is enhanced by the use of substoichiometric amounts of the vinyl ether and further, as will be shown, provides for some control over the formation of the different acetal substances as already described. It is to be noted that depending on the particular R group, acetal corresponding to Formula (III) may be volatile and susceptible to removal under the conditions employed to manufacture the composition. In this case, the end composition may not contain acetal (I) and acetal (III) type components in commensurate proportions.

Some control of the degree of formation of the first, second, and third acetal substances can be exercised by selection of reaction temperature and rates of addition of the vinyl ether to the monohydroxyl-terminated polyoxyalkylene. To promote the transacetalization reaction, the reaction temperature is, advantageously, at least 30°C, preferably from 30°C to 100°C, and more preferably from 40°C to 80°C. At higher temperatures an undesirable color of the composition can result. It is found that under the acid catalyzed conditions and elevated temperature that reaction of the vinyl ether proceeds relatively quickly and that addition times ranging from a few minutes to 10 hours, and typically from 10 minutes to 2 hours provide for essentially complete conversion of the vinyl ether. It is observed that higher rates of addition of the vinyl ether generally favor the transacetalization reaction.

Suitable monohydroxyl-terminated polyoxyalkylene substances for use in the process include an oxyalkylene adduct of a fatty alcohol having the formula:



wherein F, AO, and n are as given above. The AO moiety advantageously comprises a majority of C₂ oxyethylene, units. The term "majority", means substances wherein more than 50, preferably at least 65, more preferably at least 80, and up to 100 mole percent of the total oxyalkylene content is oxyethylene. Preferably, the monohydroxyl-terminated polyoxyalkylene contains a hydrophobic substituent having from 6 to 30 carbon atoms. A wide variety of oxyalkylated fatty alcohols are generally commercially available and obtained by the reaction of a fatty alcohol with an alkylene oxide including notably propylene oxide, butylene oxide and especially ethylene oxide, usually in the presence of an alkaline catalyst. Oxyalkylated fatty alcohols particularly well suited for use in the process of this invention are those which do not have any appreciable free salt content, as can be acquired by the in situ acid treatment of the

alkali catalyst used in the manufacture of the oxyalkylated fatty alcohol. The presence of an appreciable amount of free salt can be detrimental to the formation of acetal and eventual effectiveness of the composition in the chosen application area. If free salt is present, it is, advantageously, less than 100 ppm, and preferably less than 50 ppm of oxyalkylated fatty alcohol.

Suitable alkyl vinyl ethers for use in the process correspond to those having the general formula:



wherein R is as mentioned above; and Y, when intending to prepare an acetal adduct is hydrogen and, when intending to prepare a ketal can be any (cyclo) alkyl, aryl or heterocyclic radical but advantageously is a C₁-C₆ alkyl or aryl radical.

As mentioned, the reaction takes place in the presence of an acid catalyst. Such acid catalyst can be a free acid, such as for example p-toluene sulphonic acid. Preferably, for avoidance of its subsequent removal, the acid catalyst is present on a fixed bed in which case an acidic ion-exchange resin can be employed to advantage.

Although it is preferred to obtain the acetal or ketal containing composition directly by the above-mentioned process, it is envisaged that the final acetal/ketal content of the so obtained composition could be modified by subsequently adding a desired amount of a hydroxyl-terminated polyoxyalkylene free of any acetal/ketal substances. In a less preferred embodiment, it is also contemplated that the desired composition could be obtained by blending a pure acetal or ketal substance(s) with a hydroxyl-terminated polyoxyalkylene free of any acetal/ketal substance in the appropriate proportions.

The following examples are given to more fully illustrate the present invention. As such they are not intended to be, nor should they be construed as being, limitative of its scope in any way. All parts and percentages are based on weight unless otherwise indicated.

Example 1

Acetal-containing compositions, Compositions 1 to 4, are prepared according to the following general procedure. Amounts of substances where not mentioned in the general procedure are identified in Table I.

A reactor is charged with a given amount of an alkoxylated fatty alcohol (FAE) represented by the formula C₁₀O-(C₂H₄O)₇H, and 3.1 parts by weight of an acidic ion-exchange resin DOWEX 50 W8 available from The Dow Chemical Company. The resulting mixture is brought to a temperature of 105°C at a reduced pressure of 10 mbar and maintained under these conditions for approximately 2 hours to minimize any water content. The "dried" mixture is then brought to 50°C and ambient pressure, under nitrogen, prior to introducing a given amount of isobutyl vinyl ether (IBVE). The IBVE is introduced in one portion with continuous agitation of the mixture. After 30 minutes, the resulting reaction product is filtered to remove acidic ion-exchange resin providing a pale yellow to colorless acetal-containing

composition. Certain physical properties of the resulting acetals compositions are reported in Table I along with the relative concentrations of the acetals corresponding to Formulae I, II, and III as observed by ^{13}C NMR (CD_3COCD_3). The physical properties are observed according to the following test procedures, for: wetting times DIN 53901; foam behavior according to the
5 "Ross-Miles" test, ASTM-D-1173; and aqueous cloud point, ASTM D-2024.

The critical micelle concentration (CMC) is determined by measuring the surface tension of water at 25°C according to the Du Nuoy Ring Method in the presence of varying concentration (ppm) of the compositions. The variance of surface tension with concentration of the composition is plotted and the point at which the surface tension ceases to change
10 (decrease) with increasing concentration is taken as being the CMC value.

Example 2

Composition 5 is prepared according to the above general procedure with reactants in the proportions as indicated for Composition 2 except, in this instance, the total amount of IBVE is added in small increments over a period of 30 minutes and the resulting
15 mixture stirred for a further 30 minutes prior to removing the ion-exchange resin. Compositional analysis and physical properties of Composition 5 are also reported in Table I.

With reference to the data reported in Table I, the following comments are given. The pour point temperature of the composition increases with decreasing total acetal content of the composition. Better foam control is exhibited by compositions having a higher total
20 acetal content. The cloud point temperature of the composition generally increases with decreasing total acetal content of the composition. However, unexpectedly the cloud point can be significantly influenced by the distribution of the different acetal components. For example, Composition 5 has approximately the same total acetal content as that of Composition 2 and yet exhibits a significantly higher cloud point temperature. The ability to
25 influence cloud point in such a manner enhances the value of the compositions for applications where susceptibility to unwanted, unattractive, turbidity may be encountered.

Example 3

The biodegradability of substances is evaluated in an aerobic aqueous medium with the Manometric Respirometry test according to published OECD Guidelines for testing of
30 Chemicals Number 301F and Method C.4-D in Commission Directive 92/69/EEC. Substances are considered as being readily biodegradable if the extent of biodegradation is more than 60 percent after 28 days.

Based on oxygen consumption after 28 days, Compositions 2 and 4 exhibited a biodegradability ranging from 72 to 81 percent.

35 By way of comparison in the same valuation, a representative commercially available oxyethylene-oxypropylene C_{13} -fatty alcohol having an oxyethylene:oxypropylene weight ratio of 85:15 exhibits a biodegradability of 34 percent.

Table I

Composition	FAE pbw	IBVE pbw/ mole eq.	wt% of FAE and total acetal content in composition		Relative wt% of different acetals			Pour Point (°C)	Cloud Point (°C)	Wetting Time (sec)	Foam Behavior, " Ross-Miles" (mm)		CMC in water at 25°C (ppm)
			FAE	Acetal	I	II	III				0 min	300 min	
1	124.3	27 / 1.0	4	96	41.7	51.2	7.0	- 12.4	2.5	42	2	0	7.5
2	130.7	19.4 / 0.7	21.6	78.4	48.8	46.2	4.9	- 10	13.5	48	15	0	6
3	137.4	12.9 /0.45	40.1	59.9	57.6	39.4	3.0	- 3	28	71	20	2	3
4	143.6	6.5 / 0.2	65	35	71.5	27.2	1.2	- 4	46	44	60	8	6
5	130.7	19.4 / 0.7	26.5	73.5	9.3	89	1.6	- 10	23.9	48	10	0	/
A*	100	/	100	/	/	/	/	0	71	39	140	100	500

* Not an example of this invention

Example 4

The value of the compositions of this invention for cleaning applications, where additional control of foam formation can be important, is demonstrated by the following example where the compositions are used to substitute for a standard nonionic surfactant in a typical all-purpose cleaning formulation.

The performance of the cleaning formulation is observed according to the industrially accepted *Industrieverband fuer Putz and Pflegemittel* (IPP) test. A weighted sponge having absorbed on to it the cleaning solution is mechanically moved backwards and forwards (a total of 10 passes) over a soiled substrate, which has also been wetted with the cleaning solution. The cleaned substrate is then washed in running water before it is measured for comparative cleanliness. The "soiling" of the substrate, a clear plastic strip to which a wrinkled, white, PVC strip has been attached, consists of carbon black and oleochemicals. The cleaning efficiency, of the formulation is determined by measuring the whiteness of the cleaned substrate via the reflectance of light and comparing it to that of the original surface.

The foam control potential of the formulation is demonstrated by a modified Ross-Miles test in which 200 mL of tap water is dropped from a height of 1 meter on to 3.2 mL of the neat formulation, the initial height of foam formed is reported along with the time for its disappearance. Formulation (% by weight):

20	2.93	DOWANOL DPM an oxypropylene adduct of methanol, available from The Dow Chemical Company
	1.4	DOWANOL DPnB an oxypropylene adduct of butanol, available from The Dow Chemical Company
	1.54	Monoethanolamine
	1.4	Nonionic surfactant, see Table II
	1.2	linear alkyl benzene sulphonic acid
	0.5	Coco Fatty acid
25	0.31	Citric acid monohydrate
	3.0	Trisodium Citrate
	0.3	Magnesium Sulphate

balance to 100% being deionized water.

30

35

Table II

	Nonionic Surfactant	C mp. 1	Comp. 2	Comp. 3	Comp. 4	Com. A*
5	IPP Test (Neat Formulation)	90.5	91.7	91.3	90.4	89.9
	% surface cleaned					
10	IPP Test (1.5 wt% of formulation in tap water):	65.8	60.2	60.8	59.5	54.1
	% surface cleaned					
	Foam Control	cm	cm	cm	cm	cm
	0 Sec	1.3	1.5	1.8	1.8	2.3
15	10 Sec	0.1	0.2	0.5	0.5	1.0
	20 Sec	/	0.1	0.4	0.3	0.5
	30 Sec	/	0.1	0.3	0.2	0.3
	40 Sec	/	/	/	0.1	-
	60 Sec	/	/	/	0.1	0.1
	90 Sec	/	/	/	/	0.1

20 * Not an example of this invention

Example 5

As in Example 4, the value of the compositions of this invention as nonionic surfactants in a typical hard surface cleaner can be demonstrated. A typical hard surface cleaner formulation is given below, the nonionic surfactant is as given in Table III. Comparative

25 Surfactant C, representative of a typical commercially employed nonionic surfactant is DOWFAX 20A64, an oxypropylene-oxyethylene adduct of a fatty alcohol, available from The Dow Chemical Company.

		Formulation (% by weight):
30	3.0	DOWANOL DB an oxyethylene adduct of butanol, available from The Dow Chemical Company
	2.6	Nonionic surfactant, see Table III
	2.9	Sodium paraffin sulphonate
	0.8	K Coco soap
	0.7	Sodium hydrogen carbonate
	0.1	Sodium chloride
	1.1	Magnesium Sulphate
35		balance to 100%, deionized water

Table III

	<u>Nonionic Surfactant</u>	<u>Comp. 2</u>	<u>C*</u>
5	IPP Test (Neat Formulation) % surface cleaned	89.6	89.3
10	IPP Test (1.5 wt% of formulation in tap water): % surface cleaned	54.8	53.8
	Foam Control (at pH 8)	cm	cm
	0	11	9.5
	1 Min	9.5	9
	2 Min	5	8
15	3 Min	2.5	7.5
	4 Min	1.5	7
	5 Min	1.3	6.5

* Not an example of this invention

Example 6

20 Many cleaning formulations require the presence of a nonionic with an anionic
surfactant to provide for an optimum performance. In such formulations it is frequently highly
desirable to control and minimize foam formation and/or its persistence. This example
demonstrates, by use of the above described modified Ross-Miles Test, the surprisingly good
ability of the compositions of the invention to provide for foam control of a formulation
25 comprising an anionic and nonionic surfactant.

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	<u>pbw</u>	<u>Example 6.1*</u>	<u>Example 6.2</u>	<u>Example 6.3*</u>	<u>Example 6.4</u>
	Water	94.5	94.5	94.5	94.5
5	ANIONIC SURFACTANT:				
	DOWFAX 3B2	3.0	3.0	/	/
	Sodium Paraffin sulphonate	/	/	3.0	3.0
	NONIONIC SURFACTANT:				
10	DOWFAX 20A64 *	2.5	/	2.5	/
	Composition 1	/	2.5	/	2.5
	FOAM CONTROL: height (cm)				
	0	13.5	9	14.5	14.5
	0.5 Min	12	6	14	12
15	1 Min	11.5	1.5	13.5	9
	1.5 Min	11	1	13	8
	2 Min	10.5	0.9	12.5	7.5

* Not an example of this invention

Anionic surfactant DOWFAX 3B2 is available from The Dow Chemical Company.

20 Example 7

This example illustrates the value of the composition of this invention as a foam control agent in the food industry.

At room temperature, into a 1 weight percent solution of milk powder in water, further containing 10 ppm of a foam control agent, an air stream is introduced with agitation to produce a foam. The time taken for the foam to rise to the top of the vessel is measured. The air supply is then switched off, agitation stopped, and the time taken for the foam to collapse measured.

	<u>Foam Control Agent</u>	<u>Foam rise time (sec)</u>	<u>Foam Collapse time (sec)</u>
30	/	20	140
	Dowfax DF-115 *	195	40
35	Composition 6	300	40

* Not an example of this invention

Composition 6 retards most effectively foam formation and also provides for an attractive, short, dispersion time of foam should it accumulate. Composition 6 is obtained according to the general procedure of Example 1 by reacting an alkoxylated fatty alcohol represented by the formula $C_{10}O-(C_2H_4O)_9H$ with 0.94 mole equivalents of isobutyl vinyl ether.

- 5 The resulting composition contains 6 weight percent alkoxylated fatty alcohol and 94 weight percent of an acetal composition; the acetal composition being constituted by 43.9 weight percent Acetal-I, 50.6 weight percent Acetal-II and 5.5 weight percent Acetal-III. Composition 6 exhibits a cloud point temperature of 15°C.

- 10 Foam control agent DOWFAX DF-115, available from The Dow Chemical Company, is representative of such agents as presently used in the industry for this purpose.

The examples presented hereinabove clearly demonstrate that the compositions of the invention have an enhanced surface activity; exhibit similar or improved cleaning performance; exhibit a highly desirable degree of biodegradability; and exhibit a good degree of foam control.

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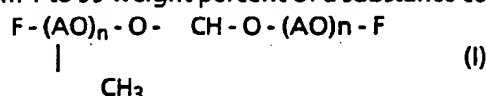
Claims:

1. A composition comprising a hydroxyl-terminated polyoxyalkylene and an acetal or ketal characterized in that the:

- a) the acetal or ketal, present in an amount of from 1 to 99 percent by weight based on total parts by weight of the composition, is an adduct of a monohydroxyl-terminated polyoxyalkylene; and
- b) the composition exhibits a critical micelle concentration (CMC) in water of less than 25 ppm of water at 25°C.

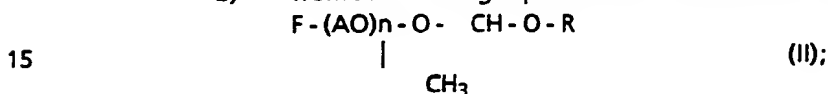
2. The composition of Claim 1 containing an acetal and wherein said acetal is a mixture which, based on total parts by weight of all acetal present, comprises:

- a) from 1 to 99 weight percent of a substance corresponding to Formula (I):



and

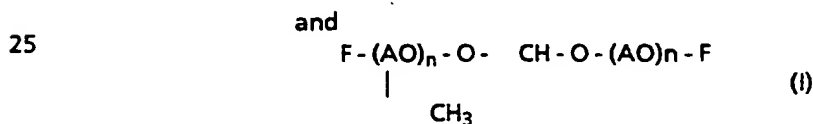
- b) from 99 to 1 weight percent of a substance corresponding to Formula (II):



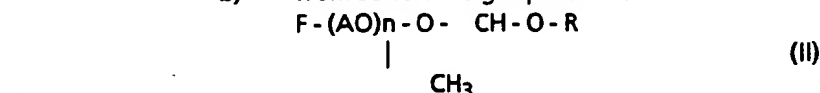
wherein F is independently a hydrocarbyl radical having from 6 to 30 carbon atoms; AO is independently a C₂₋₄ oxyalkylene moiety; n is independently a number of from 3 to 30; and R is a hydrocarbyl radical having from 1 to 5 carbon atoms.

3. A fatty alcohol alkoxylate composition that contains from 1 to 99 parts per 100 parts by total weight of the composition of an acetal mixture comprising components (a) and (b) wherein said mixture is characterized in that, based on the total parts by weight of (a) and (b) present, it comprises:

- a) from 1 to 99 weight percent of a substance corresponding to Formula (I);

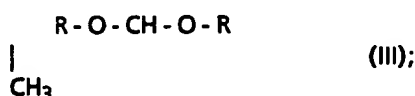


- b) from 99 to 1 weight percent of a substance corresponding to Formula (II):



wherein F is independently a hydrocarbyl radical having from 6 to 30 carbon atoms; AO is independently a C₂₋₄ oxyalkylene moiety where more than 50 mole percent of the oxyalkylene moiety is a C₂ substance; n is independently a number of from 3 to 30; and R is a hydrocarbyl radical having from 1 to 5 carbon atoms.

4. The composition of Claim 2 or 3 which further comprises, (c) a substance corresponding to Formula (III):



wherein R is a hydrocarbyl radical having from 1 to 5 carbon atoms, and which is present, based on total parts by weight of all acetal present, in from 0.1 to 15 weight percent.

5 5. A process for preparing a composition, according to Claim 2 or 3, characterized in that a monohydroxyl-terminated polyoxyalkylene or fatty alcohol alkoxylate is reacted, in the presence of an acid catalyst, with an alkyl vinyl ether present in an amount to provide from 0.05 to 0.98 equivalents per hydroxyl group.

6. A method for stabilizing oil or gas well walls which comprises using an invert-emulsion or emulsion drilling mud wherein the invert-emulsion drilling mud contains from 0.5 to 100 percent by weight, and the emulsion drilling mud contains from 0.5 to 50
10 percent by weight, of a composition according to Claim 1, 2, 3 or 4.

7. A method for dispersing oil spills on water which comprises treating an oil-contaminated water surface with a dispersing agent comprising a composition according to Claim 1, 2, 3 or 4.

8. A method for controlling foam formation of an aqueous or non aqueous
15 mixture in an environment with free surface turbulence which comprises bringing said mixture into contact with from 0.0001 to 10 percent by weight of a composition according to Claim 1, 2, 3 or 4.

9. A method to mercerize textile threads which comprises treating the textile thread with a caustic solution in the presence of a composition according to Claim 1, 2, 3 or 4.

20 10. A formulation which comprises a composition according to Claim 1, 2, 3 or 4 for use as a cosmetic agent, a cleaning agent, an oil dispersant, a foam controllant, a lubricant or a mercerizing agent.

11. A formulation which comprises a composition according to Claim 1, 2, 3 or 4, and an active component being a herbicide, insecticide, fungicide, bactericide, or a
25 physiologically active substance.

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PCT/US 95/07886

IPC 6 C08G65/32 C08L71/02 C11D1/825 C11D1/72

IPC 6 C08G C11D C08L

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 204 683 (BASF) 24 May 1974 cited in the application see claim 1 see example 1 see page 6, line 13 - line 15 ---	3,5
A	DE,A,23 02 876 (BASF) 1 August 1974 see claim 1 ---	1-11
A	DE,A,34 41 542 (HOECHST AG) 15 May 1986 see claim 1 see page 3, line 21 - line 26 ---	1-11
A	US,A,3 954 886 (LANGDON, W. K.) 4 May 1976 see claim 1 ---	1-11
	--- -/--	

☒ Patent family members are listed in annex.

- "A" document defining the general state of the art which is not considered to be of particular relevance
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28 September 1995

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INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 95/07886

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,1 164 997 (B.P. CHEMICALS) 24 September 1969 see claim 1 ---	1-11
A	WO,A,91 01171 (GAF CHEMICALS) 7 February 1991 see claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/US 95/07886

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2204683	24-05-74	DE-A- 2252186 BE-A- 806233 CH-A- 577444 NL-A- 7314700 US-I- B409310	16-05-74 18-04-74 15-07-76 29-04-74 23-03-76
DE-A-2302876	01-08-74	US-A- 3920706 BE-A- 809976 FR-A- 2322921 JP-A- 49109275 NL-A- 7400652	18-11-75 22-07-74 01-04-77 17-10-74 23-07-74
DE-A-3441542	15-05-86	EP-A- 0185898	02-07-86
US-A-3954886	04-05-76	CA-A- 1072584 DE-A- 2548142 FR-A- 2292012 GB-A- 1511177 SE-A- 7512955	26-02-80 12-08-76 18-06-76 17-05-78 24-05-76
GB-A-1164997	24-09-69	NONE	
WO-A-9101171	07-02-91	AU-B- 6035890	22-02-91

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